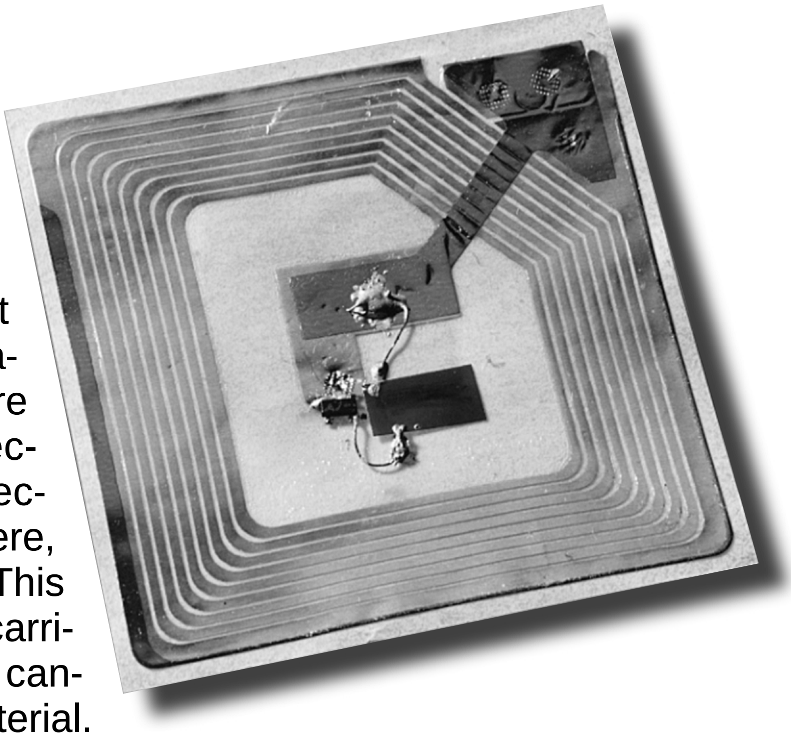
# conductive plastics

## Of luminescent plastics and plastic transistors



Plastics are polymers, that is, chains of many identical molecules (monomers) that are intercoupled. The reason that most plastics are isolators is that their electrons are localized. Each electron is firmly fixed, as it were, to its own atomic nucleus. This means that the electrons, carriers of the electric current, cannot move freely in the material.

In conductive or semiconductive plastics, discovered by accident in Japan in 1977, this is different. In these, the polymer chains have conjugated connections. This means that the discrete atoms are interconnected alternately by a single and a double chemical bond.

Based on ‘Plastic chips & luminous plastics’ a report from Philips Research

### DEVELOPMENTS TO DATE

After conductive polymers had been discovered by accident in Japan in 1977, researchers at the University of Cambridge in England discovered luminescent polymers in the late 1980s. In line with modern practice, the university hived off this discovery for commercial exploitation to Cambridge Display Technologies (CDT). The first luminescent polymer, polyphenyl-vinyl or PPV, is patented by CDT. The company has granted a licence to Philips of the Netherlands for the commercial exploitation of the polymers.

Today, CDT is developing flexible displays based on PolyLEDs and has already demonstrated a prototype of a polymer display, which was developed in cooperation with Seiko-Epson. It concerns a small, monochrome display that as yet does not consist solely of polymers: the electrodes are made of indium tin oxide (InSnO2) and aluminium (Al). Nevertheless, the performance is remarkable: its luminosity is four times as great as that of liquid-crystal displays (LCDs) and does not suffer from the limited viewing angle that is so characteristic of LCDs.

The German firm of Hoechst collaborates with Philips in the manufacture and further development of PolyLEDs. Hoechst has also joined forces with Uniax, an American firm in California which has produced the first seven-segment display consisting of PolyLEDs.

The company that succeeds in producing truly flexible displays will have the commercial world at its feet. The number of possible applications of PolyLEDs runs into the hundreds. However, the technological difficulties to market these applications are still a formidable obstacle.

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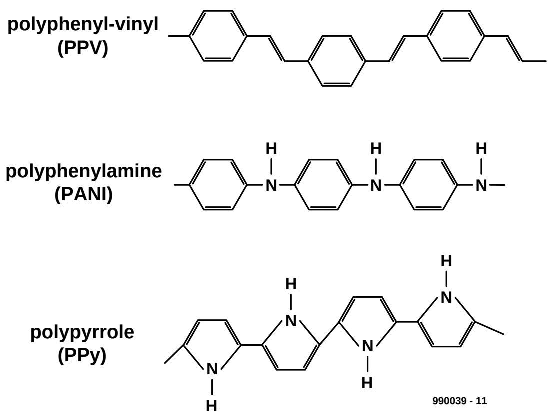

*Figure 1. Chemical structures of some often used conjugated polymers: polyphenyl-vinyl or PPV; polyphenylamine (often called polyaniline) or PANI; and polypyrrole or PPy. The polymers form long chains consisting of thousands of monomers that are coupled in tandem. Characteristic of all semiconductive polymers is their conjugated structure, which means that their bonds are alternately single and double.*

## RELEVANT PHYSICS

Conductive or semiconductive plastics are polymer chains with conjugated double links. The first PolyLEDs were based on polyphenyl-vinyl (PPV). The principle of their conductivity (or, rather semiconductivity) is best illustrated by the simplest polymer with a conjugated structure: polyacetylene. See **Figure 1**.

The single bond in the conjugated structure is always a $\sigma$-bond, whereas the double one consists of a $\sigma$-bond and a $\pi$-bond, which has a different character. Two variants of polyacetylene that differ only in the locations of the $\pi$-bonds are shown in **Figure 2**. It could be said that these variants could be merged freely. The real structure is a mixture of the variants in which each is represented equally.

This has an important consequence: in the case of an $\sigma$-bond, the electrons forming the bond are bonded to both nuclei and therefore localized. Normally, this is also the case with electrons forming a $\pi$-bond. Because of the conjugated structure, that is, a mixture as in Figure 2, the electrons are free to move along the entire chain.

This does not mean, of course, that the material itself, which consists of many monomers, becomes conductive. This occurs only when electrons can hop from one chain of polymers to another. It has been found that this becomes possible when the chains are in close proximity of each other. The closer the chains are together, the more mobile the electrons become. This is further enhanced by purification of the material and doping it, that is, adding charge carriers.

## PROCESSING

In their original state, semiconductive polymers cannot be easily processed. This is because the conjugated structure of double bonds results in flat, inelastic chains. The addition of large, flexible side chains—see **Figure 3**—renders the polymers solvent, which simplifies their processing. Varying the chemical composition of the side chains enables properties such as solubility, durability and conductivity to be enhanced.

The great benefit of conductive polymers is that the area of devices made from them is virtually limitless. Conventional semiconductor technology is heavily involved in miniaturization; silicon, the basic material, is eminently suitable in this development. The production of large devices is, however, much more complicated and expensive, because the material used must be crystalline. This means that its lattice must not contain even the tiniest distortion. The production

*Figure 2. The normal chemical notation of the structure formula of, for instance, polyacetylene, offers two possibilities. These suggest that the double bonds are localized. In reality it concerns a mixture of the two.*

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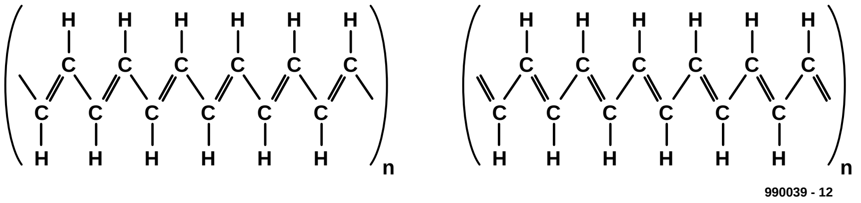

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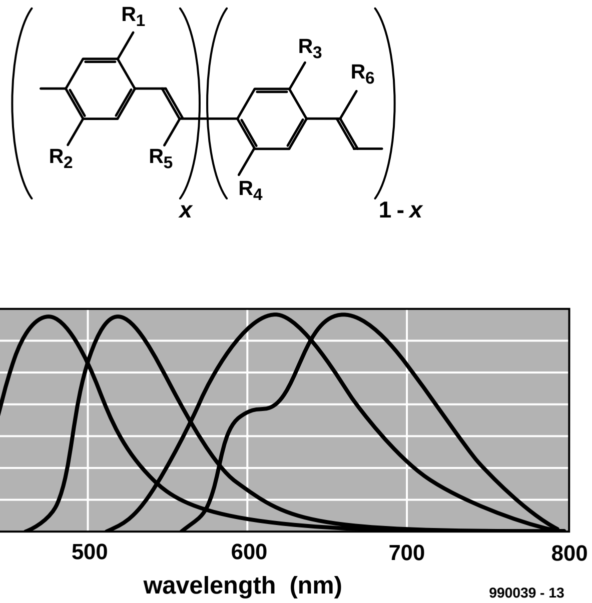

***Figure 3. The addition of side chains ($R_1$–$R_6$) to polyphenyl-vinyl (PPV) results in the emission of light in all possible colours. Each of these colours corresponds to a different chemical composition of the side chains.***

of silicon is tedious and requires accurately defined ambient conditions. The larger the crystal, the more difficult its production becomes. This is not the case with plastics, so that polymers may open the way to large semiconductor components.

## THE POLYLED

When an electric potential is applied across semiconductive plastics, they emit light. This property, discovered by researchers at the University of Cambridge in England, forms the basis of the PolyLED..

The PolyLED is essentially a much simpler component than a transistor. Its applications include segment displays such as used in mobile telephones and background lighting in liquid-crystal displays.

PolyLED technology enables the manufacture of thinner displays than is possible in liquid-crystal technology. Moreover, PolyLEDs operate with low (battery) voltage and are therefore eminently suitable for use in modern equipment.

PolyLEDs are also very thrift. Today, the luminous flux is of the order of 4–8 lm W$^{-1}$ (the picture tube in a current TV receiver emits 1 lm W$^{-1}$ and an LC display, 1.5 lm W$^{-1}$. Researchers aim to produce conductive polymers that produce a luminous flux of 25 lm W$^{-1}$. In comparison, an incandescent bulb emits about 20 lm W$^{-1}$ and a fluorescent tube about 70 lm W$^{-1}$.

A further advantage is that since light is emitted omnidirectionally, there is no limiting reading angle.

## CONSTRUCTION OF THE POLYLED

A PolyLED consists of a structure of a conductive polymer sandwiched between a cathode and an anode on a substrate of glass or transparent plastic—see **Figure 4**. The electric potential between cathode and anode ensures that a constant stream of electrons enters the polymer from the top. The drainage of electrons via the anode creates vacancies (holes) in the polymer that are mathematically equivalent to positrons (positive electrons). The incoming electrons fill these vacancies so that both hole and electron disappear. In this process, the electron emits a quantum of energy in the form of a photon.

The cathode and anode are fabricated from calcium (Ca) or indium-tin oxide (InSnO$_2$). The latter material is transparent, which is, of course, necessary if light is to be passed. The electrodes may be patterned, so that not only flat luminous structures can be produced, but also company logotypes, segments of displays, and even pixels of a display screen.

## POSSIBLE APPLICATIONS

In theory it is possible to produce a light-weight colour television screen from conductive polymers. Although this is futuristic, researchers have already succeeded in producing a matrix display with a vertical and horizontal resolution of 100 pixels on which graphics images could be represented.

All initial research was directed at the removal of technical barriers, for which orange PolyLEDs were used. Today, it is possible to fabricate red, green and blue PolyLEDs. Since these materials behave in a virtually identical manner, with these three primary colours it is possible to make polymers of any desired colour. The requisite potential across the polymer is 3–5 V and the brightness of the emitted light depends on the level of current through the material.

A durability of about 50 000 working hours has already been achieved.

## TRANSISTORS ALSO

Apart from diodes, it is also possible to make plastic transistors from conductive polymers. With reference to **Figure 5**, the transistor is deposited on a substrate of polyimide. (1).

With spin-coating*, the first electrode is deposited on to the substrate. This consists of a 200 nm thick layer of polyphenylamine (polyaniline or

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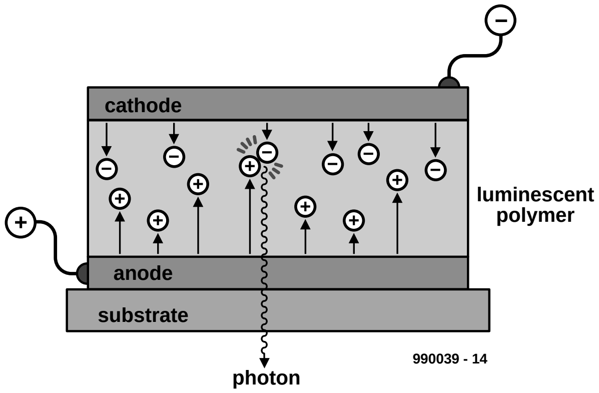

***Figure 4. A PolyLED consists of a luminous polymer sandwiched between two electrodes with the combination bonded to a substrate of glass or transparent plastic.***

PANI). The polyphenylamine is deposited in liquid form to which a photo-initiator has been added. (2).

The electrode is illuminated by ultraviolet light via a stencil. Owing to the photo-initiator, the electrical resistance of the illuminated areas increases by a factor $10^{10}$, turning the areas into isolators. The non-illuminated areas remain conductive. (3).

The electrode is heated whereby the residue of the photo-initiator evaporates. (4)

With spin-coating, the next two layers are deposited: a 50 nm thick film of semiconductive PTV and a 250 nm thick film of polyvinyl pyrrolidone (PPV—an isolator). (5)

The second polyphenylamine electrode, to which a photo-initiator has been added, is deposited by spin-coating. (6)

The second electrode is illuminated by ultraviolet light via the same stencil as used earlier. (7).

The final result is a plastic transistor which may be linked to other transistors to form an integrated circuit via a gate, source and drain. The electrical properties of the transistor are determined primarily by the PTV film. (8)

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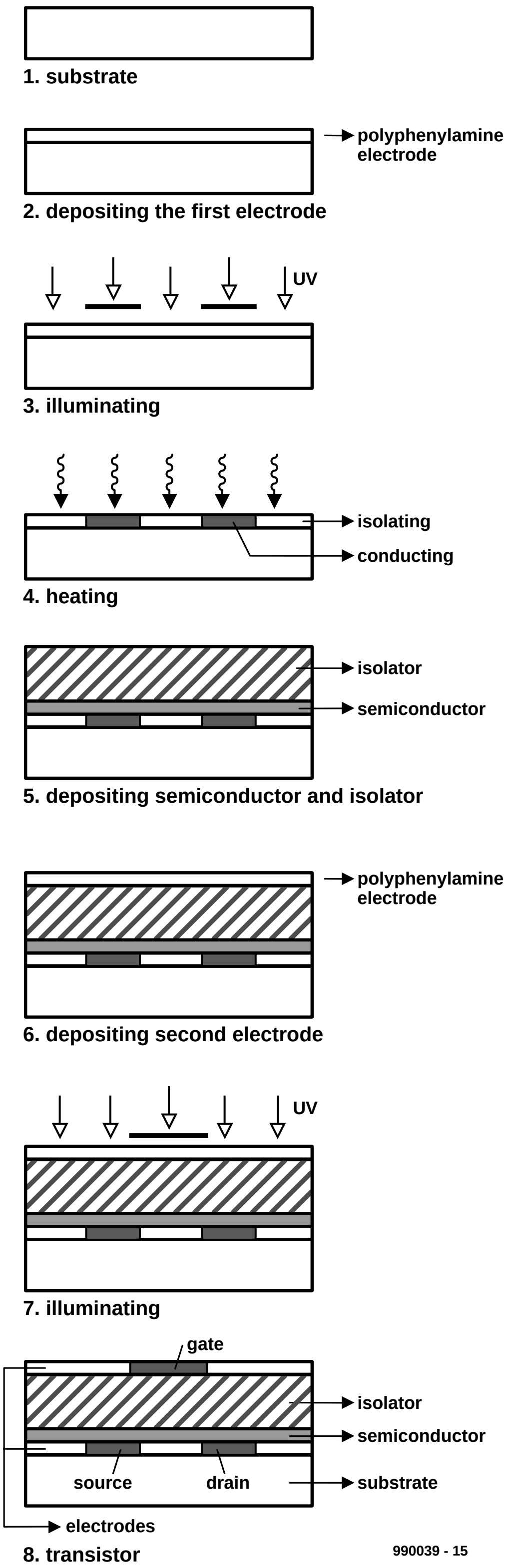
***Figure 5. A plastic transistor can be produced from conductive polymers by a step-by-step lithographic process. The end result is a four-layer wafer bonded to a polyimide substrate.***



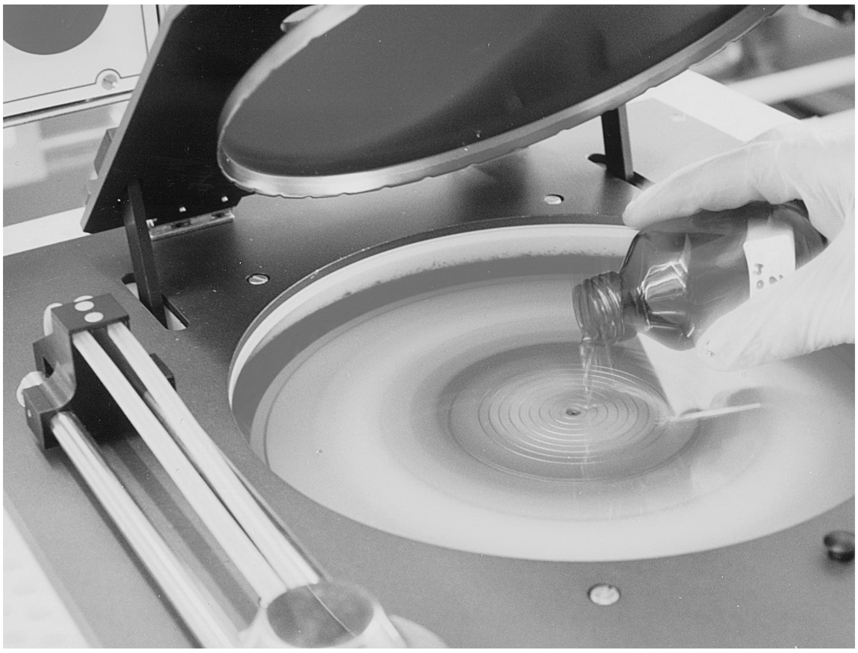


***Figure 6. Spin-coating is a technique that enables a thin film of one material (in liquified form) to be deposited on to another (solid) material.***

** Spin-coating is a technique that enables a virtually homogeneous film of liquified material 100–200 nm thick to be deposited on to another material, The solid material, such as the substrate of a diode or transistor, is made circular and the resulting disc is made to rotate at very high speed. A drop of the liquified material is dropped on to the disc and spreads out into a thin, homogeneous film. When the solvent (used to liquify the material to be deposited) has vaporized, the film solidifies. There are virtually no limitations to the size of substrate that can be used in spin-coating. See* ***Figure 6****.*
*Dip-coating is a similar process in which use is made of the bond that can be formed between substrate and film material. In this process, however, the substrate is briefly immersed into the soluble polymer.*